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RELATIONSHIP OF THE SECOND ORDER  
NONLINEAR OPTICAL COEFFICIENT TO BANDGAP IN



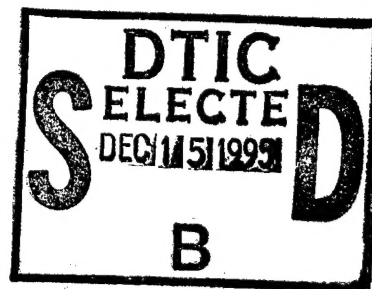
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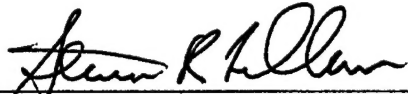
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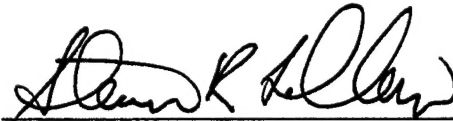
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13. ABSTRACT (Maximum 200 words)

Second order nonlinear optical coefficient data and band gap data collected from the literature have been classified and are organized by plotting their respective values. The two-dimensional plots indicate that both large bandgap - and small  $X(2)$ , and small bandgap - and large  $X(2)$  are highly correlated. A corresponding trend is also demonstrated for the figure of merit which is used to rank materials for wavelength conversion efficiency. Results of the analysis are used to estimate the second order nonlinear optical properties and conversion efficiencies of several less-well-known materials. Trend analysis suggests that ordered  $\text{GaInP}_2$  would be exceptional as a E-O waveguide material and that the FOM of  $\text{AgGaTe}_2$  is 3.6 times that of  $\text{AgGaSe}_2$  and that crystals of  $\text{HgGa}_2\text{Se}_4$  and  $\text{Te}_x\text{Se}_{(1-x)}$  alloys should be of distinct interest as wavelength conversion materials for infrared applications. The maximum attainable  $X(2)$  is in the range of 3500-4000 pm/V for bound electrons. For bandgaps less than one eV, the increase in  $X(2)$  with decreasing bandgap slows considerably.

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## INTRODUCTION

The purpose of this paper, is to provide a means of estimating and comparing the wavelength conversion efficiency (figure of merit, FOM) of new nonlinear materials knowing only their bandgap. The approach for the estimates is trend analysis of existing data<sup>1-28</sup> for the second order nonlinear coefficient,  $\chi^{(2)}_{ijk}$ , or  $d_{ij} = \chi^{(2)}_{ijk}/2$ , the index of refraction  $n$ , and the bandgap  $E$ . No underlying physical basis for the result will be presented. The result of this trend analysis, in the form of plots of  $\chi^{(2)}$  vs  $E$  and FOM vs  $E$  and the associated fit equations, will be used to estimate  $\chi^{(2)}$  and the FOM for wavelength conversion efficiency for some new materials. The accuracy goal agrees within a factor of 2-5 with the experimental values, which is quite good considering the values range over four to seven orders of magnitude.

In this paper, following the usual conventions, the  $\chi^{(2)}$  values are treated as having constant values in the region of high transparency between the bandgap and the onset of multiphonon absorption, and the full  $\chi^{(2)}$  values are used, which means the impact of the phase matching angle is ignored. The requirement to phase match often reduces significantly the effective  $\chi^{(2)}$  values below those of the full values. The distinction between direct, indirect, or pseudodirect bandgaps is ignored and the minimum room temperature gap is used in all cases.

A number of trends are now well known for semiconductors. Representative examples are: a decreasing thermal conductivity as the bandgap decreases, an increasing mobility as the bandgap decreases, an increasing spin-orbit splitting as the bandgap decreases, a decreasing bandgap as the lattice constant increases, an increasing index of refraction as bandgap decreases, an increasing dielectric constant as bandgap decreases, and increasing non-linear susceptibilities as the linear susceptibilities increase. The last three examples are relevant to the present discussion and will be described in some detail below, followed by some observations related to corresponding *ab initio* calculations.

The nonlinear optical behavior of crystals in response to intense optical beams is understood in

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terms of a nonlinear polarization<sup>11,28</sup>. The polarization tensor  $\mathbf{P}(\mathbf{E})$  is related to the electric field tensor  $\mathbf{E}$  through Eq (1) or Eq (2), where,  $\chi^{(2)}_{ij} = 2 d_{ij}$ ,  $\kappa$  is the dielectric susceptibility,  $\chi^{(2)}$  (subscripts are omitted subsequently) and  $\chi^{(3)}$  are the nonlinear susceptibility coefficients.

$$\mathbf{P}(\mathbf{E}) = \kappa(\mathbf{E}) \cdot \mathbf{E} = \kappa_0 \mathbf{E} + \chi^{(2)} \cdot \mathbf{E}^2 + \chi^{(3)} \cdot \mathbf{E}^3 + \dots \quad (1)$$

$$P_i = \kappa_{0ik} E_k + \chi^{(2)}_{ij} E_j^2 + \dots, \quad (2)$$

In Eq (2), the three dimensional tensor is written in the usual "plane" representation. In the following discussion, the subscripts will be omitted except where helpful for clarity of meaning. All non-centrosymmetric compound semiconductors will have a non-zero  $\chi^{(2)}$  and be optically transparent. Generally speaking for infrared applications, all III-V and II-VI compound semiconductors and their pseudo-ternary analogs, the I-III-VI<sub>2</sub> and II-IV-V<sub>2</sub> chalcopyrites with bandgaps of the order of 2 eV or less, have large  $\chi^{(2)}$ 's. A number of compounds from these families with  $\chi^{(2)}$ 's in the range of 66 pm/V (i.e., AgGaSe<sub>2</sub>) to the enormous value of 470 pm/V (i.e., CdGeAs<sub>2</sub>) have received serious consideration for infrared applications.

The usual FOM for wavelength conversion efficiency can be expressed as  $(\chi^{(2)})^2/n^3$ , where  $\chi$  is the effective  $\chi$ -value which depends on the specific crystal structure and the direction of the incident optical beam on the crystal and  $n$  is the index of refraction in the transparent region. For the zinc blende or the chalcopyrite semiconductors the appropriate  $\chi$  is  $\chi_{36}$ . It is traditional to compare  $\chi^{(2)}$  values only and ignore the issue of beam direction in first order comparisons of the nonlinear optical properties. In this paper trend analysis of  $\chi^{(2)}$  vs bandgap and FOM vs bandgap is used to estimate the size of  $\chi^{(2)}$  and the FOM for wavelength conversion efficiency for known and unknown materials.

A trend between index of refraction and bandgap was pointed out by Moss<sup>27</sup> in 1950. The

Moss expression for the index of refraction  $n$ , where the constant has been slightly modified by Ravindra and Srivastava<sup>26</sup>, is given as Eq (3), where the energy in this and subsequent equations is in eV:

$$n = (108/E)^{1/4} \quad (3)$$

The data compiled and modeled by Phillips<sup>29</sup> and VanVechten<sup>30</sup> presented a corresponding relationship between the dielectric constant  $\epsilon$  or linear susceptibility  $\chi^{(1)}$  and energy gap, as pointed out by Soref<sup>31</sup>, as the Moss-like relationships of Eqs (4) and (5).

$$\epsilon = (a/E)^{1/2} \quad (4)$$

or

$$\chi^{(1)} = (b/E)^{1/2} \quad (5)$$

where  $a$  and  $b$  are appropriate constants. Considering that  $n^2 = \epsilon$ , Eq (4) has the same functional form as Eq (3). The physical basis for Eq (4), Eq (5), and by inference Eq (3), is provided within the framework of the Phillips' bond charge model<sup>29,30</sup>.

Miller<sup>32</sup> in 1964 noticed that the  $\chi^{(2)}$  values available for eleven materials could vary by several orders of magnitude from material to material. He found to his surprise that the  $\chi^{(2)}$  is proportional to a product of the three linear susceptibilities. This relationship is now known as Miller's Empirical Rule and the proportionality constant is known as Miller's  $\delta_{ij}$ . Flytzanis<sup>33</sup> states that, in a certain sense, this rule was the first hint that nonlinear susceptibilities could be expressed in terms of other macroscopic properties. If the mean value of  $\delta_{ij}$  determined for these 11 materials is used, then all of the  $d$  values can be calculated to within a factor of two. The rule can also be written in terms of indices or dielectric constants. For indices the rule can be written<sup>31</sup> in rationalized mks

units:

$$\chi^{(2)} = 2(8.85 \times 10^{-12})(n_{\omega}^2 - 1)(n_{2\omega}^2 - 1)(\delta_{ij}), \quad (6)$$

where  $\chi^{(2)}$  is in m/V and  $n_{\omega}$  and  $n_{2\omega}$  are the indices respectively at the frequencies  $\omega$  and  $2\omega$ . Miller's original constant value for  $\delta_{ij}$  in his units was 0.38 and the specific value for GaAs was 0.24. Using the presently accepted value of 180 pm/V for  $\chi^{(2)}$  gives a value for Miller's delta of 0.0246 in rationalized mks units, which yields

$$\chi^{(2)} = 0.436 (n_{\omega}^2 - 1)(n_{2\omega}^2 - 1), \quad (7)$$

where the units of  $\chi^{(2)}$  are pm/V.

Subsequently, Flytzanis and Ducuing<sup>34</sup>, in a study of the specific material-to-material variation of  $\delta_{ij}$  within the III-V semiconductor family, found that Miller's delta correlates remarkably well with the dipole moment of the cation-anion bond. Ultimately, using the bond charge model, Levine<sup>35</sup> provided an approach for calculating the value of  $\delta_{ij}$  for a given material. Levine's value for  $\delta_{ij}$  used in conjunction with Miller's Empirical Rule overestimates the experimental values by 20% or less for a large number of semiconductors. This modification based on physical insight greatly improved the accuracy of Miller's Empirical Rule. However, it was Miller's Empirical Rule that provided the insight for the establishment of the underlying physical basis for nonlinear optical susceptibility.

Ignoring dispersion, Miller's Empirical Rule, as given by Eq 7, reduces approximately, for large index materials, for  $n^2 \gg 1$ , to :

$$\chi^{(2)} = (0.436) n^6 (\delta_{ij}), \quad (8)$$

Combining Miller's rule, Eq (6), and the Moss relationship, Eq (3), indicates that for  $\chi^{(2)}_{ij}$  increases rapidly as E decreases, going as  $(1/E)^{3/2}$ . In the same spirit, the FOM also increases rapidly as E decreases, going as  $(1/E)^{9/4}$ . Tabulations of  $\chi^{(2)}$  values versus transparency range given by Prokhorov<sup>37</sup>, or of the FOM for wavelength conversion versus transparency range given by Shay and Wernick<sup>38</sup> for representative materials, also suggest the trend that nonlinear properties increase rapidly with decreasing bandgap. The prior successes of empirical property trend analysis have served as the motivation for the FOM trend analysis to follow.

The alternate approach of *ab initio* calculations of the corresponding quantities, particularly for even-order susceptibilities like  $\chi^{(2)}$ , is presently not generally feasible. Flytzanis<sup>33</sup> has reviewed efforts to produce approximate theoretical scaling laws for nonlinear susceptibilities and Levine et al.<sup>39</sup> and Zhong et al.<sup>40</sup> have made "near" *ab initio* calculations of the nonlinear susceptibilities. These two approaches are discussed below.

Flytzanis has shown that odd order nonlinear susceptibilities, like the linear one can be cast in the form of scaling laws, essentially power laws of an effective parameter which turns out to be a measure of the valence electron delocalization and can be expressed in terms of measurable macroscopic quantities. It is found that for three-dimensional systems the odd order susceptibilities scale as:

$$\chi^{(2m-1)} = (P^2)(1/E^{(3m-1)}), \quad (9)$$

where P is the average transition-dipole-moment matrix element and  $m = 0, 1, 2, \dots$ . For  $\chi^{(1)}$  and  $\chi^{(3)}$  Eq (9) gives

$$\chi^{(1)} = P^2/E^2 \quad (m = 1) \quad (10)$$



and

$$\chi^{(3)} = (P^2)(1/E^5). \quad (m = 2) \quad (11)$$

Note that the ratio of  $\chi^{(1)}$  to  $\chi^{(3)}$  yields  $\chi^{(3)} = \chi^{(1)}/E^3$ . Eq (10) may be compared to Eq (5), implying that  $P^2$  scales as  $E^{-3/2}$ , for  $\chi^{(1)}$  scaling as  $E^{-1/2}$ , and that  $\chi^{(3)}$  scales as in Eq (12) below:

$$\chi^{(3)} = (c)(1/E)^{6.5}, \quad (12)$$

where  $c$  is an appropriate constant. These scaling laws were derived in the one-electron approach, ignoring electron correlations via a critical point analysis. These scaling laws might become invalid as the average atomic number of the compound increases to the point that spin-orbit-splitting is a significant portion of the gap. This occurs for very narrow gap materials.

Sheik-Bahae et al.<sup>36</sup> used a two band model to calculate the scaling of  $\chi^{(1)}$  and found that empirically an  $E^{-4}$  dependence is successful in predicting the  $\chi^{(3)}$  for a wide variety of semiconductors and insulators over four orders of magnitude. This is a somewhat slower but similar dependence to the  $E^{-6.5}$  dependence given by Eq (12).

It is not possible<sup>33</sup> to provide a similar approximate theoretical expression for even-order susceptibilities such as  $\chi^{(2)}$  because it is sensitive to local properties of the electron density, and integration over the entire Brillouin Zone is required. The physical basis is that the simultaneous requirement for large charge asymmetry and large charge delocalization are competing processes resulting in some cancellation effects. However, the empirical trend for  $\chi^{(2)}$  and the approximate theoretical scaling laws for odd order susceptibilities indicate that, generally, susceptibilities are a power law function of the bandgap, increasing rapidly as the bandgap decreases.

The "nearly" *ab initio* calculations of the nonlinear susceptibilities for some III-V compounds and Se have been reported<sup>37,38</sup>. At present *ab initio* calculations do not accurately predict the bandgap, tending to produce a value about 1.0 eV too small and a lattice constant 0.100 to 0.200 nanometers too small. Unfortunately, the value of  $\chi^{(2)}$  is extremely sensitive to lattice

constant/bond length and bandgap<sup>37</sup>. These limitations are overcome by adding a constant self-energy correction to the Hamiltonian to fix the bandgap and using the experimental lattice parameters. This "nearly" *ab initio* approach then gives good agreement with experimental results for compounds of elements in and above Period IV. However, for elements and compounds in Period V or greater such as Te, CdGeAs<sub>2</sub>, and InSb, this approach does not apply, as once again spin-orbit-splitting has not yet been taken into account. The results for the five materials for which  $\chi^{(2)}$  was calculated also shows the general trend that  $\chi^{(2)}$  increases rapidly with decreasing bandgap. Fitting the data indicates that  $\chi^{(2)}$  increases as  $E^{-3}$  and FOM as  $E^{-6}$ .

Flytzanis<sup>33</sup> points out that the searches for scaling laws and empirical trend analysis for susceptibilities, as for other physical properties, serves many purposes, fundamental as well as practical. They allow the prediction of the properties of new materials by simple inspection, they introduce economy in comparing materials, and they help formulate guidelines for the search for new materials, as well as provide guidance for the development of theory by singling out dominant mechanisms. In the general case, scaling laws and empirical trend analysis are the only tools available for guiding new materials development.

## RESULTS AND DISCUSSION

Using a database compiled from the literature for a number of compounds of interest for nonlinear optical applications, a plot of the second order nonlinear coefficient,  $\chi^{(2)}$ , versus bandgap has been constructed, and is given in Figure 1. A similar plot of the FOM versus bandgap is given in Figure 2. Where known or observed, uncertainty for these values was noted; otherwise a minimum of  $\pm 20\%$  relative error was assumed, a value most likely too small an error for much of the data in view of the wide variability observed from the literature where some error ranges approach factors of two. In converting from relative to absolute values the value of  $\chi^{(2)/36} = 180$  pm/V from reference 14 has been used following general practice. We note that many values

reported in the literature have been converted using much higher values ranging from 139 to 151, which give values larger by 50% to 70%. In Table 1, Soref's  $\chi^{(2)}$  values for IV-IV compounds are used. These are calculated values assuming Miller's rule and using  $\delta_{ij}$  for SiC. This approach, in view of the saturation shown in Figure 1, may overestimate significantly the  $\chi^{(2)}$ 's of the narrow bandgap members of the family such as GeSn.

The general trend of both  $\chi^{(2)}$  and FOM is to increase rapidly with decreasing bandgap. In Table 1 are listed the data (and sources) used in the plots. Examination of the curves shows that a single power law expression cannot represent the data well over the total bandgap range. Regression fits were computed which relate  $\chi^{(2)}$  to bandgap and FOM to bandgap for a single curve over the full range of E, and two curves. The least squares fits are listed in Table 2. A power law was chosen because it is consistent with the results of the ones discussed in the introduction, although  $\chi^{(2)}$  also can be fit reasonably well an  $e^{-E}$  type law ( $\chi^{(2)} = 1134e^{-1.1E}$ ). Clearly, the single curve overestimates large band gap compounds, while underestimating small band gap compounds. For those materials with gaps from about 0.8 to about 3 eV, the single curve fit provides an order of magnitude estimate. The two curves provide better estimates for the ranges 0 to about 1 eV and 1 to about 8 eV. We note that the Miller's  $\delta$  values are rather widespread for this set of compounds, covering a range of about a factor of two, and having an average value of about  $0.05 \text{ m}^2/\text{C}$ .

Calculated values based on Table 2 and actual values are listed in Table 3 for several well known materials. Table 3 indicates that predictions are within a factor of two in the IR for both  $\chi^{(2)}$  and FOM, and over the full range all agree approximately within the goal of a factor of 2-5. Further comparisons are presented in Tables 4 and 5. In Table 4, predicted values and actual values for families are compared by calculating ratios for three groupings, using the lowest value of the group as a reference. The results are presented in columns 5 and 6, and they suggest that the predicted values are close to the actual values where known. Again the accuracy is within a factor of two in the IR. In Table 5 a similar comparison is made for FOM. The results indicate reasonable agreement except for the narrow band, where the predicted value severely underestimates the actual

value, although the agreement with the relative value is within a factor of two. Also, we note that predicted values of FOM may be in error by factors more than two, because  $\chi^{(2)}$  enters FOM as the square. The trend, however, is valid for FOM.

The fits in Table 2 are applied to four promising relatively unknown materials; 1) the recently discovered ordered ternary III-V compound GaInP<sub>2</sub>, predicted by Wei and Zunger<sup>41</sup> for which no nonlinear properties are available, 2) the less well known AgGaTe<sub>2</sub> whose nonlinear properties have not been reported and which is a member of the compound family whose two well known members are AgGaS<sub>2</sub> and AgGaSe<sub>2</sub>, 3) several new members of the II-III<sub>2</sub>-VI<sub>4</sub> family, defect or pseudo chalcopyrites, which includes the well known mercury thiogallate, HgGa<sub>2</sub>S<sub>4</sub>, and 4) TeSe solid solution alloys which have not received the consideration they deserve as very high efficiency materials. These Equations are also applied to three well known materials, GaAs, ZnGeP<sub>2</sub> and CdGeAs<sub>2</sub> as baseline comparisons. All of these results are presented in Table 5. As a final discussion, several additional subtrends based on families of compounds are discussed.

Random ternary alloy III-V semiconductors have received little attention, although their  $\chi^{(2)}$ s can be very large, because they are isotropic, and, therefore, do not possess birefringence which is necessary for conventional wavelength conversion processes. However, in the ordered state it would be expected that ternaries like GaInP<sub>2</sub> would be birefringent uniaxial crystals. Stenger et al.<sup>42</sup> have experimentally verified this expectation of adequate birefringence by variable angle spectral ellipsometry measurements for CuPt-like ordering in GaInP<sub>2</sub>. The estimated  $\chi^{(2)}$  from Table 4 for ordered GaInP<sub>2</sub> is 130 pm/V, a value large in practical terms. This seems to be a very reasonable value, since it is somewhat less than the trend value for GaAs of 214 pm/V, as would be expected from its slightly larger bandgap, and the trend result for GaAs is in fairly good agreement with the literature<sup>19</sup> value of 180 pm/V. It would seem that films of ordered GaInP<sub>2</sub> would be exceptional waveguide materials.

Some years ago, Bell et al.<sup>43</sup> investigated the properties of the AgGaTe<sub>2</sub> compounds and commented that AgGaTe<sub>2</sub> had good mechanical properties and should have a sufficiently large birefringence to be useful for nonlinear optics, although there had not been any studies of this

aspect of the AgGaTe<sub>2</sub> compounds. Because  $\chi^{(2)}$  data for AgGaTe<sub>2</sub> is not available from the literature, the estimated value from Table 4 is 233 pm/V. Comparing trend results with literature values for AgGaS<sub>2</sub> and AgGaSe<sub>2</sub> indicates that, for this family, the trend result overestimates the literature values but does accurately reflect the relative values for these two materials as shown in column VII of Table 4. In Figure (1), the II-VI compounds and their pseudo-ternaries lie generally lower while following the same slope which is consistent with the actual materials dependence of Miller's  $\delta$ . Relying on the more reliable relative value would give a  $\chi^{(2)}$  of 101 pm/V which exceeds the value for AgGaSe<sub>2</sub> by 60% and more importantly a factor of 3.5 times greater FOM. This material is certainly worth re-exploring.

Radautsan et al.<sup>44</sup> have surveyed a number of the II-III<sub>2</sub>-VI<sub>4</sub> compounds and indicate that their nonlinear properties are interesting. The thiogallates HgGa<sub>2</sub>S<sub>4</sub>, HgGa<sub>2</sub>Se<sub>4</sub>, HgIn<sub>2</sub>Se<sub>4</sub> are compared using Table 2 and the bandgaps reported by Radautsan et al. The trend result of 36.2 pm/V for  $\chi^{(2)}$  for HgGa<sub>2</sub>S<sub>4</sub> is in reasonable agreement with the literature value<sup>11</sup> for  $\chi^{(2)}$  which ranges from 53.6 pm/V to 70.4 pm/V. So the trend results listed in Table (3) should be reasonable estimates. For HgIn<sub>2</sub>Se<sub>4</sub>, the estimate for  $\chi^{(2)}$  is an impressive 196 pm/V, its FOM is a factor of 15 larger than that of HgGaS<sub>4</sub>! Its range of transparency should be quite large, given its calculated range is from 0.86 microns to much greater than 12 microns, the long-wavelength cut-off of HgGa<sub>2</sub>S<sub>4</sub>.

Tellurium has the second highest reported  $\chi^{(2)}$  for a semiconductor and it is transparent in the infrared. However, in CO<sub>2</sub> laser doubling experiments it has been found that two photon absorption and intraband scattering of free carriers limits its application to low power levels. This is a result of its narrow bandgap. This problem could be alleviated by alloying with Se to increase the bandgap. Pure tellurium crystals are quite soft and deformation induced defects also limit its performance<sup>45</sup>. Alloy hardening may adequately improve its mechanical properties. The optical properties of Te crystals alloyed with respectively 2%, 2.7%, and 11% have been reported<sup>46,47</sup>. There is evidence that a solid solution exists for all concentrations<sup>46</sup> where the lattice constant decreases in a linear fashion as selenium is added to tellurium. The bandgaps in eV and the

respective short wavelength cut-offs in microns for the 0%, 2.7%, 11%, and 100% cases are respectively 0.358/3.46, 0.375/3.3, approximately 0.4/3.1, and 1.7/0.72. Alloying provides a method of continuously varying the cut-off from 3.46 to .72 microns. The  $\chi^{(2)}$  and the FOM will vary with composition as the bandgap varies as indicated by Eq (4) and (5), but this dependence may be nonlinear, as pointed out by Stuke and Keller<sup>48</sup>. Thus, a linear interpolation of band gap values from pure Te and pure Se based on composition will yield incorrect results. Using the bandgap composition results of Stuke and Keller, for a 1 eV bandgap/1.24 micron cut-off alloy, the composition  $\text{Te}_{.286}\text{Se}_{.714}$  is required. Once a bandgap value is estimated,  $\chi^{(2)}$  and FOM can be read from the plots; in this case, this compound has a  $\chi^{(2)}$  of about 700 pm/V and FOM of about  $3000 \text{ pm}^2/\text{V}^2$ .

The intraband scattering mechanism mentioned above which limits the performance of Te will be much less severe in the alloys. As the bandgap is widened the valence band splitting is significantly smaller in comparison, and this scattering mechanism is much less important. In addition, Dubinskaya<sup>46</sup> reports an approach which may overcome this limitation. Te and, by analogy, these alloys are easily bleached to improve their transparency in the infrared by exposing the crystals to weak visible light sources. The impressively large values for the nonlinear parameters indicate that a serious exploration of this alloy system is warranted.

The power law dependencies for FOM and  $\chi^{(2)}$  are summarized in Table 6 and discussed below. Empirically, the FOM depends more strongly on E than  $\chi^{(2)}$  does. As a result, reducing the bandgap is significantly more beneficial than the  $\chi^{(2)}$  trend alone might indicate. From the fit for  $\chi^{(2)}$  in the bandgap range  $> 1 \text{ eV}$ , and from the "nearly" *ab initio* calculation for the 1.4 - 2.45 eV range, the bandgap dependences are similar, as  $m = 2.6$  and 3, respectively. For the FOM the "nearly" *ab initio* result and our results give respectively  $m = 6$  and  $m = 4.1$  (using our large gap value) or  $m = 0.9$  using our small gap value, indicating that the field dependence of FOM is overestimated by the calculated results.

For bandgaps  $< 1 \text{ eV}$ , the bandgap dependence for both FOM and  $\chi^{(2)}$  are strikingly lower as saturation sets in. A comparison of "nearly" *ab initio* results for the narrow bandgap materials has

not been made, because the model does not include spin-orbit-splitting and it is useful only for compounds made up of low atomic number atoms<sup>49</sup>. The bond charge model, the approximate *ab initio* model, and the "nearly" *ab initio* model fail to predict the saturation observed for FOM and  $\chi^{(2)}$ , although Miller's rule does, as shown in Figure 1. However, Miller's rule does poorly in the wide bandgap regime, tending to overestimate significantly. At the present time the bandgap dependence over the full range is treated successfully only by trend analysis, which covers materials with a gap of less than one eV.

A more careful look at the trends in Fig. (1) indicates that the data can be grouped in a number of ways to identify sub-trends. Compounds with Group V or VI anions can be grouped as the upper or high bandgap group while oxides and complex structures as the lower or low bandgap group. Using these groupings, there are at least two curves present -- one for narrow bandgap and one for large bandgap. Several compound families show similar slopes when the anion element is considered, for example, {ZnS, ZnSe, ZnTe}, {CdS, CdSe, CdTe}, {GaP, GaAs, GaSb}, {CuGaS<sub>2</sub>, CuGaSe<sub>2</sub>}, {Se, Te} and {AgGaS<sub>2</sub>, AgGaSe<sub>2</sub>} have similar slopes. The sulfides and the selenides tend to fall below the trend line, for the III-V compounds, in agreement with their smaller Miller's  $\delta$ 's. The II-IV-V<sub>2</sub> family members, on the other hand, tend to fall above the trend line for the III-V compounds, in agreement with their large Miller's  $\delta$ 's. The {CdGeP<sub>2</sub>, CdGeAs<sub>2</sub>} line has a lower slope than the others, as does {ZnS, CdS, HgS}. The {InP, InAs, InSb} trio does not lie on a line, suggesting that the data may be suspect, probably for the InAs, because the line for InP and InSb has a slope similar to that for similar groupings. The predicted value for In As is about 1650 pm/V  $\pm$  500. If the {CdGeP<sub>2</sub>, CdGeAs<sub>2</sub>} data is correct, this suggests that the  $\chi^{(2)}$  value for ZnGeAs<sub>2</sub> should be about 356 pm/V  $\pm$  75 based on the direct bandgap value of about 1.15 eV. However, it is anticipated that ZnGeAs<sub>2</sub> will not possess an adequate birefringence, because its tetragonal distortion is zero (i.e.,  $c/a = 2.0$ ).

## CONCLUSIONS

As a means for quickly estimating the value of a material, these curves offer a simple and direct means for classifying nonlinear optical materials. The plots show a strong trend in the data, i.e.,  $\chi^{(2)}$  increasing rapidly with decreasing bandgap. The FOM depends more strongly on E than  $\chi^{(2)}$  does, and, as a result, reducing the bandgap is significantly more beneficial than the  $\chi^{(2)}$  trend alone might indicate. The bandgap dependence of the "nearly" *ab initio* and that of our empirical result for the bandgap near and above one eV are identical. A saturation of  $\chi^{(2)}$  at band gaps below one eV is observed in our empirical trend, although the various models described fail to predict this behavior, and trend analysis is superior to Miller's rule for large bandgaps. This relationship alone is of value in estimating  $\chi^{(2)}$  for a compound based on band gap value. Thus, a non-centrosymmetric compound can be evaluated in broad terms as to its utility as a  $\chi^{(2)}$  nonlinear optical material. Trend analysis indicates that films of ordered GaInP<sub>2</sub> would be exceptional as E-O waveguide materials, that the FOM of AgGaTe<sub>2</sub> is an impressive factor of 3.5 times greater than that of AgGaSe<sub>2</sub> and crystals of HgGa<sub>2</sub>Se<sub>4</sub>, and that Te<sub>x</sub>Se(1-x) alloys are of distinct interest, because they are very efficient wavelength conversion materials for infrared application.

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**Table 1. Data used to plot  $\chi^{(2)}$  against band gap. Sources of the data are given in the references listed at the bottom of the table.  $\delta_{ij}$  = Miller's delta; Index = index of refraction. Units are Gap in eV,  $\chi$  in pm/V, FOM in (pm/V)<sup>2</sup> and  $\delta_{ij}$  in m<sup>2</sup> /C.**

	Compound	Ref No.	Gap	$\chi^{(2)}$	FOM	Index	$\delta_{ij}$
1	InSb	a,b	0.23	3268.0	43322.43	3.95	0.056
2	Te	c	0.33	1300.0	3834.71	4.794	0.007
3	GeSn	a,p,q	0.36	2308.0	14614.17	4.5	0.02
4	InAs	a,d	0.36	838.0	4388.84	3.42	0.033
5	CdGeAs <sub>2</sub>	c,e,f	0.57	820.0	3821.59	3.5	0.029
6	GaSb	d	0.72	1256.0	7785.99	3.7	0.028
7	SiSn	a,p,q	0.84	1010.0	4138.01	3.95	0.02
8	SiGe	a,p,q	0.9	674.0	2224.02	3.71	0.02
9	SnC	a,p,q	1.2	556.0	1656.46	3.6	0.02
10	AgInSe <sub>2</sub>	c,e,g,h	1.2	100.0	135.87	2.6	0.031
11	InSe	a	1.25	200.0	131.19	4.2	-
12	InP	d	1.35	287.0	505.86	3.4	0.008
13	GaAs	b,d	1.4	270.0	521.22	3.27	0.011
14	CdTe	a,c,i	1.5	336.0	1551.50	2.63	0.077
15	CuInS <sub>2</sub>	c,e,j,k	1.53	19.2	5.43	2.6	0.007
16	CuGaSe <sub>2</sub>	c,e,h,j,k	1.7	70.0	60.87	2.7	0.020
17	Se	b,c	1.7	159.2	344.36	2.64	0.042
18	CdGeP <sub>2</sub>	c,e,f	1.72	320.0	788.62	3.2	0.025
19	ZnSiAs <sub>2</sub>	c,e,f	1.74	180.0	244.89	3.2	0.016
20	AgGaSe <sub>2</sub>	c,e,g,h,k	1.8	95.0	126.90	2.6	0.030
21	CdSe	c	1.8	104.0	183.87	2.5	0.047
22	Ag <sub>3</sub> SbS <sub>3</sub>	c	1.93	28.0	9.53	2.7	0.006
23	Ag <sub>3</sub> AsS <sub>3</sub>	a	2	50.0	31.75	2.7	0.012

24	GaSe	c	2.021	128.0	186.59	2.8	0.029
25	ZnGeP2	c,e,f	2.05	150.0	185.21	3.1	0.020
26	HgS	b	2.1	100.0	142.24	2.6	0.029
27	GeC	a,p,q	2.1	76.0	75.02	2.68	0.02
28	AgAsS2	a	2.14	50.0	40.00	2.5	0.022
29	b-SiC	a,p,q	2.26	60.0	51.80	2.59	0.005
30	GaP	c,d,m	2.3	200.0	335.67	3.1	0.020
31	ZnTe	a,c,i	2.3	184.4	431.89	2.7	0.043
32	CuGaS2	c,e,g, h,j,k	2.43	22.0	7.93	2.5	0.011
33	CdS	c	2.485	88.0	181.82	2.2	0.071
34	GaS	a	2.5	279.0	988.68	2.7	-
35	map	l	2.6	12.6	11.76	1.5	-
36	AgGaS2	c,g,h,k	2.638	28.0	14.18	2.4	0.022
37	ZnSe	c,m	2.7	156.8	444.63	2.4	0.077
38	AgI	c	2.8	20.0	5.50	2.6	0.021
39	CuBr	a	2.91	16.0	8.00	2.0	0.033
40	CuI	a	2.95	16.0	5.26	2.3	0.017
41	pom	l	3	6.0	2.20	1.6	-
42	CdGa2S4	a	3.05	50.0	51.37	2.3	0.030
43	CuCl	a	3.17	14.0	7.14	1.9	0.043
44	ZnO	a,b,c	3.3	3.6	0.44	2.0	0.008
45	ZnS	c	3.9	61.2	76.96	2.3	0.066
46	LiIO3	b	4	11.1	2.67	2.3	-
47	LiNbO3	b	4	10.9	4.40	1.9	0.004
48	urea	l	5.9	2.0	0.24	1.6	-
49	SiC	n	6	17.2	3.93	2.7	-

50	AlN	a	6.2	7.7	1.85	2.0	-
51	BBO	l	6.3	1.2	0.09	1.6	-
52	KDP	o	7	0.9	0.06	1.5	0.030
53	SiO <sub>2</sub>	b	8.4	0.8	0.04	1.5	0.015

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All  $\chi^{(2)}$  and Miller  $\delta$  data, except IV-IV compounds, are from *the CRC Handbook on Laser Science and Technology, Vol. III*, Ed. Martin J. Weber, CRC Press, Boca Raton, FL, 1986.

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**Table 2. Summary of Numerical Fit Equations for  $\chi^{(2)}$  (pm/V) and for figure of merit (FOM) (pm/V)<sup>2</sup> for E = 0-8 eV (full gap range), 0-1 eV (narrow gap range), and 1-8 eV (wide gap range).**

<b>Full Gap Range:</b>	$\chi^{(2)} = 291E^{-1.92}$	<b>correlation coef = 0.9</b>
<b>Narrow Gap Range:</b>	$\chi^{(2)} = 663E^{-.89}$	<b>correlation coef = .88</b>
<b>Wide Gap Range:</b>	$\chi^{(2)} = 510E^{-2.6}$	<b>correlation coef. = 0.78</b>
<b>Full Gap Range:</b>	<b>FOM = 666E<sup>-3.0</sup></b>	<b>correlation coef. = 0.86</b>
<b>Narrow Gap Range:</b>	<b>FOM = 2324E<sup>-1.4</sup></b>	<b>correlation coef. = 0.85</b>
<b>Wide Gap Range:</b>	<b>FOM = 1760E<sup>-4.1</sup></b>	<b>correlation coef. = 0.76</b>



**Table 3. Predicted  $\chi^{(2)}$  (pm/V) and FOM (pm/V)<sup>2</sup> values compared with actual values for the three line fits for compounds representative of narrow, mid, and wide energy gap values.**

$\chi^{(2)}$ :

<b>E</b>	<b>Full</b>	<b>Narrow</b>	<b>Wide</b>	<b>Actual</b>	<b>Compound</b>
<b>0.23</b>	<b>4.91E+03</b>	<b><u>2.45E+03</u></b>	<b>2.26E+04</b>	<b><u>3.27E+03</u></b>	<b>InSb (narrow)</b>
<b>1.4</b>	<b>1.52E+02</b>	<b>4.91E+02</b>	<b><u>2.14E+02</u></b>	<b><u>1.80E+02</u></b>	<b>GaAs (mid)</b>
<b>7.0</b>	<b>6.88E+00</b>	<b>1.17E+02</b>	<b><u>3.37E+00</u></b>	<b><u>1.00E+00</u></b>	<b>KDP (wide)</b>

**FOM:**

<b>E</b>	<b>Full</b>	<b>Narrow</b>	<b>Wide</b>	<b>Actual</b>	<b>Compound</b>
<b>0.23</b>	<b>5.61E+04</b>	<b><u>1.84E+04</u></b>	<b>7.65E+05</b>	<b><u>4.33E+04</u></b>	<b>InSb (narrow)</b>
<b>1.4</b>	<b>2.41E+02</b>	<b>1.45E+03</b>	<b><u>4.37E+02</u></b>	<b><u>2.32E+02</u></b>	<b>GaAs (mid)</b>
<b>7.0</b>	<b>1.88E+00</b>	<b>1.51E+02</b>	<b><u>5.63E-01</u></b>	<b><u>1.00E-01</u></b>	<b>KDP (wide)</b>

Table 4. Comparison of the calculated and literature values of  $\chi^{(2)}$ . Calculated values from equations in Table 2.

Compound	E (eV)	$\chi^{(2)}$ -Est. (pm/V)	$\chi^{(2)}$ -Exp** (pm/V)	Rel. $\chi^{(2)}$ Calculated	Exp	Estimated/ Exp Value
GaInP <sub>2</sub>	1.7	130	-	-	-	-
GaAs	1.4	214	180	-	-	1.19
AgGaS <sub>2</sub>	2.73	38.3	28	1.00	1.00	1.37
AgGaSe <sub>2</sub>	1.83	107	95	2.79	3.39	1.13
AgGaTe <sub>2</sub>	1.356	233	(170)*	6.08	-	-
HgGa <sub>2</sub> S <sub>4</sub>	2.79	36.2	53.6, 70.4	1.00	-	0.56, 0.42
HgGa <sub>2</sub> Se <sub>4</sub>	2.1	75.3	-	2.08	-	-
HgIn <sub>2</sub> Se <sub>4</sub>	1.45	196	-	5.41	-	-
Se	1.7	130	159	1.00	1.00	0.82
Te <sub>.286</sub> Se <sub>.714</sub>	1	510	(624)*	3.92	-	-
Te	0.33	1780	1300	13.69	8.18	1.37
ZnGeP <sub>2</sub>	2	85.4	150	1.00	1.00	0.57
CdGeAs <sub>2</sub>	0.57	1090	820	12.76	5.47	1.33

\*\*Reference 11

\*Calculated using ratio, e.g., 233/38.3 = 6.08; 28\*6.08 = 170.

**Table 5. Comparison of calculated and literature values for the Figure of Merit.**  
**Calculated values from equations in Table 2.**

Compound	E (eV)	FOM-Calc (p m/V) <sup>2</sup>	FOM-Exp (p m/V) <sup>2</sup>	Relative FOM Calculated	FOM Exp.	Estimated/ Exp Value
GaInP <sub>2</sub>	1.7	196	-	-	-	-
GaAs	1.4	437	232	-	-	1.88
AgGaS <sub>2</sub>	2.73	27.6	23.4	1.00	1	1.18
AgGaSe <sub>2</sub>	1.83	144	127	5.22	5.43	1.13
AgGaTe <sub>2</sub>	1.356	498	(422)*	18.04	-	-
HgGa <sub>2</sub> S <sub>4</sub>	2.79	25.2	-	1.00	-	-
HgGa <sub>2</sub> Se <sub>4</sub>	2.1	81.7	-	3.24	-	-
HgIn <sub>2</sub> Se <sub>4</sub>	1.45	378	-	15.00	-	-
Se	1.7	196	511	1.00	1	0.38
Te <sub>.286</sub> Se <sub>.714</sub>	1	1760	(4589)*	8.98	-	-
Te	0.33	11000	10,048	56.12	19.66	1.09
ZnGeP <sub>2</sub>	2	99.9	185	1.00	1	0.54
CdGeAs <sub>2</sub>	0.57	5120	3822	51.25	20.66	1.34

\*Calculated using ratio

**Table 6. Power-law scaling summary, where  $m$  is the bandgap power dependence.**

<b>FOM</b>	<b><math>m</math></b>		
	<b><math>\chi^{(2)}</math></b>	<b>Bandgap Range (eV)</b>	<b>Reference</b>
<b>3.0</b>	<b>1.9</b>	<b>8 - 0</b>	<b>this work</b>
<b>4.1</b>	<b>2.6</b>	<b>8 - 1</b>	<b>this work</b>
<b>1.4</b>	<b>0.9</b>	<b>1 - 0</b>	<b>this work</b>
<b>6</b>	<b>3</b>	<b>1.4 - 2.45</b>	<b>"nearly" <i>ab initio</i>, refs. 37, 38</b>

### Figure Captions:

Figure 1. Plot of the second order nonlinear coefficient,  $\chi^{(2)}$ , versus bandgap for a number of chalcopyrites and selected other types of compounds. See Table 1 for specific data. The “nearly” *ab initio* results (dashed line) and values calculated using Miller’s empirical rule, as given by equation 7, are plotted for comparison. open boxes: narrow gap; open circles: wide gap; x: Miller’s rule; filled diamonds: *ab initio* calculated values; the solid lines are fits for each range; the dotted line is the fit for *ab initio* values.

Figure 2. Plot of the figure of merit (FOM) versus bandgap for a number of chalcopyrites and selected other types of compounds. The “nearly” *ab initio* result (dashed line) is shown for comparison. Open boxes: narrow gap; open circles: wide gap; filled diamonds: *ab initio* values; solid lines: fits for two ranges; dotted line: fit for *ab initio* values.

